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Crystal structure and imperfection of the perovskite-like proton conductor $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$

The crystal structure complex oxide $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$ in anhydrous and hydrated forms was studied by the method of neutron diffraction, the preferred localizations of protons were set. The hydration process with temperature variation and the partial pressure of water vapor was studied. It is established that the crystallographic non-equivalence of OH-groups in the structure determines their different thermal stability. The quasi-chemical approach was proposed that describes the formation of proton defects in oxides with structural disordering.

Keywords: neutrongramma; quasichemical approach; high temperature proton conductors (HTPC).

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Introduction

Proton conductors are widely used as components of electrochemical devices such as gas sensors, electrolyzers, fuel cell membranes, etc [1–3]. The class of high temperature proton conductors (HTPC) is presented of complex oxide compounds with perovskite structure ABO_3 or derived from it. In HTPC hydrogen is not part of chemical formula, its appearance in the structure of the complex oxide is provided by the equilibrium with $\text{H}_2\text{O}/\text{H}_2$ -containing atmosphere and is described as the process of dissociative dissolution of water vapor/hydrogen [4]. Since the presence of oxygen vacancies is the main factor responsible for the appearance of proton defects, the value of the proton conductivity is determined by the complex oxide defectiveness.

In complex oxide compounds with the structural typical disorder of the oxygen sublattice, in contrast to phases with impurity disordering, the number of vacancies in the oxygen sublattice may be considerably higher, therefore the high oxygen deficiency is able to provide a significant level of concentration of protons (and therefore, proton conductivity) [5]. Such features allow us to consider these compounds as a distinct class of proton conductors and suggest the need to devise new ways to describe them. At the same time, a combination of properties, such as high concentrations of protons and high reversibility of the processes of hydration, gives ground to consider this class of proton conductors as a promising matrix for proton transport.

In the present work we report a detailed study of the crystal structure of proton conductor $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$ and set the preferred places of localization of pro-

tons, and also developed a quasichemical approach to describe the processes of formation of proton defects.

Experimental part

The synthesis of the sample with a nominal composition of $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11}$ was conducted by solid-phase synthesis from the pre-dried carbonates and niobium oxide at temperature endurances 800–1000–1200–1300 °C for 24 h with intermediate chafing. The hydrated samples were obtained by slow cooling (1 °C/min) with 1000 °C to 150–200 °C in the humid air ($p\text{H}_2\text{O} = 2 \cdot 10^{-2}$ atm). The amount of absorbed water was controlled by the method of thermogravimetry.

The neutron diffraction studies were performed at the nuclear research reactor IVV-2M (Zarechny town, Sverdlovsk region) using diffractometer D-7A with a double monochromator. The first monocrystal is pyrolytic graphite with a reflective plane (002), the second is germanium, the reflection plane is 511. The wavelength of monochromatic neutrons is $\lambda = 1.5255$ Å. Data were obtained at room temperature in the angular range 9–130 °C with a step of 0.05 °C and angular resolution is $\Delta d/d = 0.02$ %. The refinement of crystal structure was carried out using full-profile analysis on Rietveld by using the software package FullProf [6].

Results and discussion

According to the results of local energy-dispersive x-ray microanalysis it is established that the stoichiometry of the synthesized sample was maintained within 1 at. %, there was a slight variation in the values of ratios of Ba:Ca:Nb, the over-

The studies of surface morphology of the samples was performed by scanning electron microscope JEOL JSM-6390LA. For the quantitative determination of the elemental composition of the samples the energy dispersive microanalysis with energy dispersive console JEOL JED 2300 was carried out. The limit of detection at normal energies (5–20 kV) was ~0.5 at. %. The error of concentration measurement is ± 2 %. The management, monitoring and analysis of the received data were carried out using the software package Analysis Station JED series, Version 3.7.

The thermogravimetric studies were carried out in the heating process in the atmosphere of dry Ar in thermoanalyzer TG STA 409 PC (NETZSCH) included with unit quadrupole mass spectrometer QMS 403C Aëlos. The shooting of isothermal dependences of the mass from the partial pressure of water vapor was performed with stepwise change of humidity from $p\text{H}_2\text{O} = 3 \cdot 10^{-5}$ atm to $p\text{H}_2\text{O} = 2 \cdot 10^{-2}$ atm. Under each value of the activity of water vapor the system was maintained to a state of equilibrium within a few days.

all composition of the sample was characterized by a slight lack of Ca.

The study of the morphology of the powder sample did not reveal the presence of impurity phases, the homogene-

ous distribution of metal components was observed.

The structure of the anhydrous sample Ba₄Ca₂Nb₂O₁₁ was investigated by using neutron diffraction. Fig. 1 shows experimental, calculated and differential profiles of neutronography.

It is established that the crystal structure Ba₄Ca₂Nb₂O₁₁ is described in the structural type of the double perovskite A₂(BB')O₆, and is characterized by a cubic cell with space group *Fm* $\bar{3}$ *m*, which corresponds well with x-ray diffraction stud-

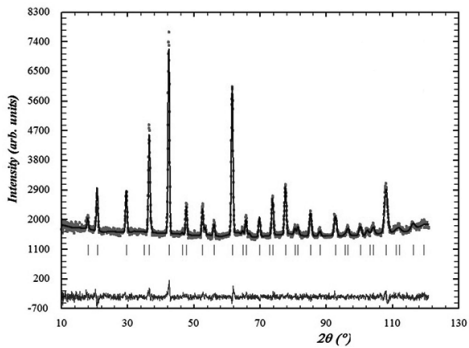


Fig. 1. Neutronogram sample composition Ba₄Ca₂Nb₂O₁₁, shows the experimental (points), calculated (line) and difference (bottom) data and the angular position of the reflexes for cubic phases (strokes)

ies carried out previously [7]. For four formula units A₂(BB')O₆ the following distribution of hydrogen atoms in the positions is characterized: 8c-crystallographic positions are filled with cations of barium (A-sublattice), the cations B-sublattice (niobium and calcium) occupy two crystallographically nonequivalent positions 4a and 4b, the oxygen takes position 24e. The main results of calculations are presented in table 1. According to the data about the coordinates of the atoms and the unit cell parameters the interatomic distances were calculated (table 2). The structure is built from connected by vertices different octahedra NbO₆ and CaO₆ formed by orderly arranged atoms of niobium and calcium and is oxygen-deficient, which is confirmed by the partial filling of oxygen positions. The location of oxygen vacancies is statistical, as the predominant places of their localization have not been identified.

The next step was the study of the structure of the sample Ba₄Ca₂Nb₂O₁₁ in hydrated form. The degree of hydration was established according to data of thermogravimetry, the overall composition is corresponded to the formula Ba₄Ca₂Nb₂O₁₁·0.96H₂O.

Table 1

The coordinates and isotropic thermal parameters (B) atoms of the anhydrous sample Ba ₄ Ca ₂ Nb ₂ O ₁₁						
atom	position	The coordinates of the atoms			coefficient of filling	B×100, Å ²
		x	y	z		
Nb	4a	0	0	0	1.00	0.5(1)
Ca	4b	0	0	0.5	0.935(2)	1.76(4)
Ba	8c	0.25	0.25	0.25	1.00	1.59(9)
O	24e	0.2347(5)	0	0	0.917(5)	2.54(8)
R _{wp} =5.14% R _p =6.06% χ ² =1.36 R(F ²)=3.37						

Characteristics of atoms:

Space group *Fm* $\bar{3}$ *m*, cubic symmetry, Z=4

The unit cell parameters: a = b = c = 8.4428(3) Å; a = b = c = 90°; V = 601.80(3) Å³; X-ray density 5.47 g/cm³

Table 2
Interatomic distances (Å) in the coordination polyhedra in the anhydrous sample

Interatomic distances	Ba ₄ Ca ₂ Nb ₂ O ₁₁		
	BaO ₁₂	CaO ₆	NbO ₆
M–O	2.987	2.222	1.999
O–O		3.142	2.827

Based on the data of neutron diffraction it was found that when hydrated niobate of barium-calcium the cell symmetry is reduced to monoclinic and can be described in the space group $P2_1/n$. Neutrongramma is presented in Fig. 2.

As a result of absorption of water is the filling of oxygen vacancies by oxygen atoms from the water molecules, respectively, the total content of oxygen in hydrated sample increases, as evidenced by the corresponding fill coefficients. Thus there is a distortion of the octahedra and the position of the oxygen atoms become non-equivalent. The data for the atomic coordinates and interatomic distances are in tables 3, 4. As

can be seen, the distance from the atom of niobium up to four equatorial oxygen atoms is equal to 2.013 Å and 2.115 Å, and to the axial atoms is 2.066 Å. In Ca-octahedron these distances are slightly larger, respectively, to the equatorial oxygen atoms is 2.226 Å and 2.125 Å, and to the axial atoms is 2.254 Å.

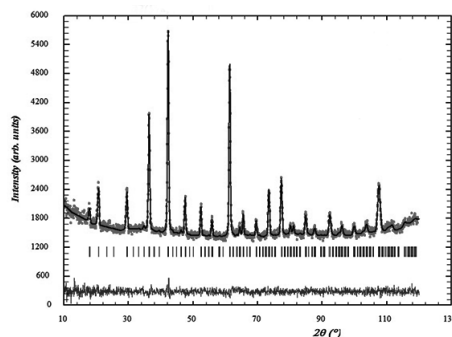


Fig. 2. Neutrongramma of sample Ba₄Ca₂Nb₂O₁₁·0.96H₂O shows the experimental (points), calculated (line) and difference (bottom) data and the angular position of the reflexes for monoclinic phase (strokes)

The coordinates and isotropic thermal parameters (B) atoms in Ba₄Ca₂Nb₂O₁₁·0.96H₂O according to data of neutron

Atom	Position	The coordinates of the atom			Filling (abs.ed)	B×100, Å ²
		<i>x</i>	<i>y</i>	<i>z</i>		
Ba	4e	−0.01312	−0.00354	0.7422	4.00	1.893(2)
Nb	2d	0.50000	0.00000	0.00000	2.00	0.889(1)
Ca	2c	0.50000	0.00000	0.50000	1.815(7)	0.989(4)
O1	4e	0.24055	0.26523	0.49187	4.000(0)	2.705(3)
O2	4e	0.24067	−0.24146	0.49764	4.000(0)	3.069(8)
O3	4e	−0.02101	0.47958	0.73512	3.616(0)	1.13(11)
H1	4e	0.10214	0.47503	0.63517	0.764	1.13(11)
H2	4e	0.27941	0.15590	0.20102	0.366	1.13(11)
H3	4e	0.07867	0.19818	0.09212	0.727	1.13(11)

$R_{wp}=3.16\%$; $R_p=4.80\%$; $R_f=5.39\%$; $\chi^2=1.36$

Characteristics of atoms:

Space group $P2_1/n$, monoclinic symmetry

The unit cell parameters: $a = 5.9864(3)$ Å; $a = b = 90^\circ$; $b = 5.9964(0)$ Å; $c = 89.838(15)^\circ$; $c = 8.4958(2)$ Å; $V = 304.97(3)$ Å³; X-ray density of 5.42 g/cm³

The position of the protons is described by three possible positions H1, H2, H3. Most of the protons (H1 and H2) is localized on axial oxygen atoms O3, forming OH⁻-groups in which the distances oxygen-hydrogen are as follows: 1.125 Å, 1.219 Å (Fig. 3). The H3 protons are localized at the equatorial oxygen atoms, shifting slightly above and below the equatorial plane and forming OH⁻-groups with a sufficiently large connection lengths of 1.37 Å (bond O2-H3). The positions of the H2 have a small filling, the main part of protons is distributed on the positions H1 and H3, which have approximately the same population (table 4).

Table 4

Interatomic distance (Å) in the structure $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11} \cdot 0.96\text{H}_2\text{O}$			
polyhedron	M–O1	M–O2	M–O3
CaO_6	2.226 (×2)	2.124 (×2)	2.254 (×2)
NbO_6	2.012(×2)	2.115(×2)	2.006 (×2)
BaO_{12}	3.068	2.941	3.098
	3.109	3.164	2.899
	2.885	2.861	2.798
	2.945	3.032	3.203
$d\text{O–H}$			
O3–H1	1.125		
O3–H2	1.219		
O2–H3	1.371		

Based on the data for fill factors, it can be concluded that there is a good correlation with the results of energy dispersive x-ray microanalysis on quantitative composition phase. The general formula can be written as $\text{H}_{1.86}\text{Ba}_4\text{Ca}_{1.82}\text{Nb}_2\text{O}_{11} \cdot 0.96\text{H}_2\text{O}$ or by highlighting hydroxo group $\text{Ba}_4\text{Ca}_{1.82}(\text{OH})_{1.86}\text{Nb}_2\text{O}_{7.14}$.

The hydration processes were studied by the method of thermogravimetry under the variations of temperature and

partial pressure of water vapor in the gas phase pH_2O (Fig. 4, 5).

On TG curves (Fig. 4) there has been a dramatic change in mass of the sample at a temperature of 400–450 °C, which

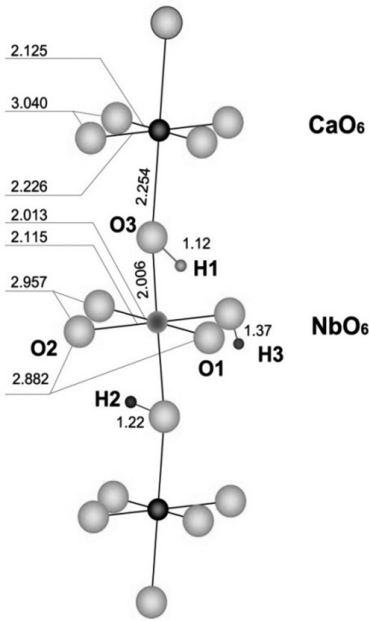


Fig. 3. The fragment structure of the sample $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11} \cdot 0.96\text{H}_2\text{O}$; shows the main interatomic distances (Å) in the NbO_6 octahedra and CaO_6 and the positions of the protons H1, H2, H3

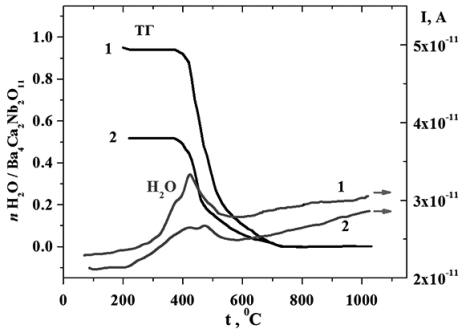


Fig. 4. TG curves and mass spectrum (ion current) water allocations in (1) $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11} \cdot 0.95\text{H}_2\text{O}$ and (2) $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11} \cdot 0.50\text{H}_2\text{O}$ (partial hydration)

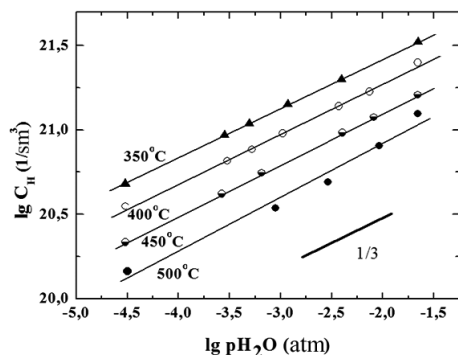


Fig. 5. The dependence of the concentration of proton defects in the structure $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11} \cdot n\text{H}_2\text{O}$ from partial pressure of water vapor

removed the main amount of water (0.65 mole), next there were more monotonous change in mass of up to 700 °C.

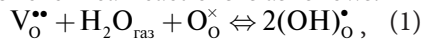
The mass spectrum characterizing the allocation of water, for extremely hydrated composition $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11} \cdot 0.96\text{H}_2\text{O}$ is presented by a peak in the temperature range 250–550 °C, its complex type indicates the superposition of several signals and reflects the presence of three overlapping effects. The mass spectrum of the allocation of water of partially hydrated sample $\text{Ba}_4\text{Ca}_2\text{Nb}_2\text{O}_{11} \cdot 0.5\text{H}_2\text{O}$ shows the redistribution of the peak intensities, primarily a decrease in intensity of low temperature peak of the allocation of water.

The crystallographic non-equivalence of the OH⁻-groups is manifested in their different thermal stability. The isolated OH⁻-groups, that are remotest from the adjacent oxygen atoms at distances comparable to the size of the octahedron, are the most thermally resistant, and this fact reflects the greatest strength of bond O–H.

The dependences of the concentration of protons from the partial pressure of water vapor $\lg C_H = f(\lg p_{H_2O})$ is presented in

Fig. 5. As you can see, in the area of investigated temperatures range 300–500 °C and $p_{H_2O} = 3 \cdot 10^{-5} \div 2 \cdot 10^{-2}$ atm there is an increase in the concentration of protons with increasing p_{H_2O} , the dependences in a logarithmic scale are characterized by a linear function with a slope of 1/3.

To describe the process of dissociative dissolution of water vapour in a matrix of complex oxide we used the quasichemical approach, which allows to demonstrate the dependence of the concentration of proton defects from atmospheric humidity. The quasichemical description of the process of water absorption is sufficient detailed described for perovskite-like phases, in which oxygen vacancies are set acceptor doping. In these views, the formation of proton defects is considered as the appearance of the proton localized on oxygen, so it is represented as a particle OH⁺, which occupies the anionic site (OH)⁺_O. The corresponding equation of quasi-chemical reactions is as follows:

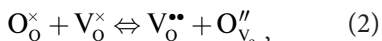


where $V_O^{\bullet\bullet}$ – the oxygen vacancy, O_O^{\times} – the oxygen atom in the regular position, $(OH)_O^{\bullet+}$ – hydroxyl group in the oxygen sublattice with an effective positive charge.

Accordingly, the concentration of proton defects in the structure of the oxide increases with increasing partial pressure of water vapor as $[OH_O^{\bullet+}] \propto p_{H_2O}^{1/2}$ ($T = \text{const}$), where $[OH_O^{\bullet+}]$ is the concentration of the defect. Usually the experimentally observed functional dependence $\lg C_H = f(\lg p_{H_2O})$ (C_H – volume concentration of proton defects) for acceptor doped perovskites $\text{ABO}_{3-\delta}$ is characterized by the slope $d \lg C_H / d \lg p_{H_2O} \approx 1/2$ [8].

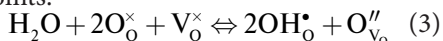
For phases with the structural disordering of the oxygen vacancies should be considered as *neutral* defects (vacant

oxygen positions), therefore the water implementation process should be described otherwise. However, the emergence of neutral defects in quasi-chemical reactions creates uncertainty, since the concentration of this neutral defect cannot be made in the condition of electroneutrality (CEN), and therefore it is impossible to establish its functional relationship with the concentrations of other defects. To avoid this situation it is usually proposed to take into account the equilibrium of the type:



where the formation of doubly ionized oxygen vacancies $\text{V}_\text{O}^{\bullet\bullet}$ occurs as a result of the migration of lattice oxygen on the place of structural vacancy, while the oxygen atom becomes formally effective negative charge corresponding to the charge of an atom in interstitial positions $\text{O}_{\text{V}_\text{O}}''$ [9]. Thus, the implementation process of the water is reduced to the equation (1).

The experimental results obtained in the present work on studying of dependency $\lg C_\text{H} = f(\lg p\text{H}_2\text{O})$ for Ba₄Ca₂Nb₂O₁₁ with structural disordering showed that a previously proposed model cannot describe the observed dependence with a slope of 1/3. Therefore, the following cases of dissociative dissolution of water in the matrix of the complex oxide with the structural disordering of the oxygen sublattice are considered below. If we consider the process of introducing water with the participation of oxygen vacancies as a neutral defect, it can be assumed that oxygen from water molecules is embedded in the place of structural vacancy, and the protons are placed at regular oxygen positions:



The condition of electroneutrality (CEN) can be written as: $2[\text{O}_{\text{V}_\text{O}}''] = [\text{OH}_\text{O}^\bullet]$. The electronic defects are excluded from the CEN, because it determines the conditions for dominance of atomic disordering. In addition, there is an additional relationship between the concentrations of neutral defects and oxygen vacancies. If we assume that initially, in the complex oxide the volumetric concentration of oxygen vacancies is characterized by some constant value, then the introduction of water it decreases as: $A - [\text{O}_{\text{V}_\text{O}}''] = [\text{V}_\text{O}^\times]$.

The equilibrium constant of reaction (3) can be written as follows:

$$K = \frac{[\text{OH}_\text{O}^\bullet]^2 \cdot [\text{O}_{\text{V}_\text{O}}'']}{p\text{H}_2\text{O} \cdot [\text{V}_\text{O}^\times]} = \frac{[\text{OH}_\text{O}^\bullet]^2 \cdot [\text{O}_{\text{V}_\text{O}}'']}{p\text{H}_2\text{O} \cdot (A - [\text{O}_{\text{V}_\text{O}}''])} \quad (4)$$

For analysis of the dependence of concentration of defects at a variation $p\text{H}_2\text{O}$ ($T = \text{const}$) we consider the conditions of approximation, corresponding to the three possible cases.

1) The low $p\text{H}_2\text{O}$

$$[\text{V}_\text{O}^\times] \approx A; \gg [\text{O}_{\text{V}_\text{O}}''], [\text{OH}_\text{O}^\bullet]$$

2) The middle $p\text{H}_2\text{O}$

$$2[\text{O}_{\text{V}_\text{O}}''] = [\text{OH}_\text{O}^\bullet] \gg [\text{V}_\text{O}^\times]$$

Since $[\text{O}_{\text{V}_\text{O}}''] < A$, then the concentration of defects will be:

$$[\text{O}_{\text{V}_\text{O}}''] < A, = (2AK)^{1/3} \cdot (p\text{H}_2\text{O})^{1/3}$$

$$[\text{OH}_\text{O}^\bullet] = (AK/4)^{1/3} \cdot (p\text{H}_2\text{O})^{1/3}$$

$$[\text{V}_\text{O}^\times] = A - (AK/4)^{1/3} \cdot (p\text{H}_2\text{O})^{1/3}$$

That is, the concentration of dominant defects will be proportional $p\text{H}_2\text{O}^{1/3}$.

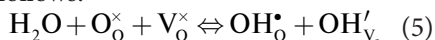
3) The high $p\text{H}_2\text{O}$

In the case of complete filling of oxygen vacancies as a result of the implementation of the water we have: $2[\text{O}_{\text{V}_\text{O}}''] = [\text{OH}_\text{O}^\bullet] = 2A, \gg [\text{V}_\text{O}^\times]$. That is, the concentration of dominant defects do not depend on $p\text{H}_2\text{O}$

Fig. 6a presents the dependence of concentration of defects from $p\text{H}_2\text{O}$ in logarithmic coordinates.

Thus, it can be expected that at low temperatures the concentration of proton defects will increase with increasing $p\text{H}_2\text{O}$ and in logarithmic coordinates it will have a slope of 1/3. In experiments on study of conductivity as a function $p\text{H}_2\text{O}$, additionally taking that the mobility of the protons is much higher than the mobility of oxygen vacancies, in the simplest case, we should also expect the increase in the total conductivity as a function $p\text{H}_2\text{O}^{1/3}$.

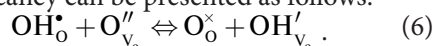
The presented calculations for structural models of the oxygen vacancies show a contrast to the case of the introduction of water in complex oxides with impurity disordering. It should say that the equation (3) describing the penetration of water into structurally disordered complex oxides is not only. The appearance of oxygen on the place of structural vacancy as the defect with a negative charge O_{V_0}'' creates conditions the preferential localization of the proton on the oxygen. Therefore, in the framework of the quasichemical formalism, this process can be written as follows:



As can be seen, the formation of two types of proton defects with different charges takes place: localization of the proton on the oxygen, standing in a regu-

lar position, leads to the appearance of the defect OH_0^\bullet , and on the oxygen coming from water molecules leads to the appearance OH'_{V_0} . The seeming contradiction related to the appearance of proton defects of opposite sign occurs because in the quasichemical description the defect is attributed to an effective charge which is determined as a differential value relative to the charge of the corresponding structural element in an ideal lattice, which is taken for zero. This writing means that the position of the protons is energetically different.

The possibility of reaction of proton exchange between lattice oxygen ions and oxygen ions, which has taken structural vacancy can be presented as follows:



We write equilibrium constants for reactions (5) and (6):

$$K = \frac{[\text{OH}_0^\bullet] \cdot [\text{OH}'_{\text{V}_0}]}{p\text{H}_2\text{O} \cdot [\text{V}_0^\times]} = \frac{[\text{OH}_0^\bullet]^2 \cdot [\text{O}_{\text{V}_0}'']}{p\text{H}_2\text{O} \cdot (A - [\text{O}_{\text{V}_0}''])} \quad (7)$$

The condition of electroneutrality can be written as: $2[\text{O}_{\text{V}_0}''] + [\text{OH}'_{\text{V}_0}] = [\text{OH}_0^\bullet]$. An additional relationship between the concentrations of defects and structural oxygen vacancies can be represented as: $[\text{V}_0^\times] = A - ([\text{O}_{\text{V}_0}''] + 1/2[\text{OH}'_{\text{V}_0}])$.

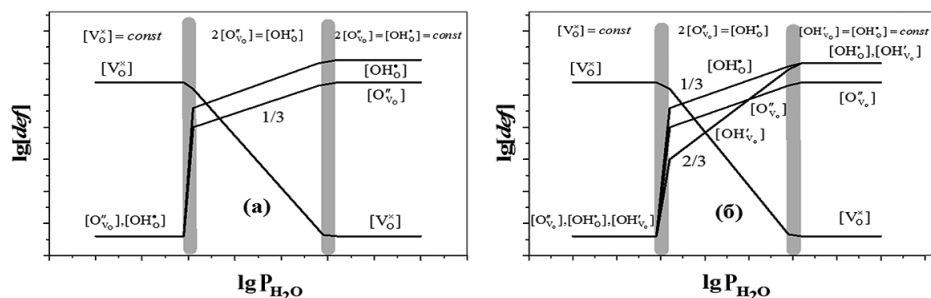


Fig. 6. The dependence of defects concentration from $p\text{H}_2\text{O}$ (double logarithmic coordinates) for models of defect formation in equations (3) and (5)

The conditions of approximation will be represented by three possible cases ($p\text{H}_2\text{O} = \text{var}$, $T = \text{const}$).

1) **The low $p\text{H}_2\text{O}$**

$$[\text{V}_\text{o}^\times] \approx A \gg [\text{O}_{\text{V}_\text{o}}''], [\text{OH}_\text{o}^\bullet], [\text{OH}_{\text{V}_\text{o}}'].$$

2) **The middle $p\text{H}_2\text{O}$**

$$2 [\text{O}_{\text{V}_\text{o}}''] = [\text{OH}_\text{o}^\bullet] \gg [\text{OH}_{\text{V}_\text{o}}']$$

$$[\text{OH}_\text{o}^\bullet] \sim (p\text{H}_2\text{O})^{1/3}$$

$$[\text{O}_{\text{V}_\text{o}}''] \sim (p\text{H}_2\text{O})^{1/3}$$

$$[\text{OH}_{\text{V}_\text{o}}'] \sim (p\text{H}_2\text{O})^{2/3}.$$

3) **The high $p\text{H}_2\text{O}$.** In the case of complete filling of oxygen vacancies as a result of introduction of water we have: $[\text{OH}_{\text{V}_\text{o}}'] = [\text{OH}_\text{o}^\bullet] \approx 2A$. That is, the concentration of dominant defects does not depend on $p\text{H}_2\text{O}$. The concentration $[\text{V}_\text{o}^\times]$ is low, a $[\text{O}_{\text{V}_\text{o}}''] \approx A$. Fig. 6b shows the calculated dependences in logarithmic coordinates.

Comparing the diagrams, it is seen that in general both approaches give a similar situation: the bulk of experimental data of the dependence of the concentration of proton defects from $p\text{H}_2\text{O}$ in loga-

rithmic coordinate will be described by a slope of 1/3 with a gradual withdrawal to the plateau at high partial pressures of water vapor.

Thus, the differences in the quasi-chemical approaches of the description of oxygen vacancies formally define the different functional dependence of the concentration of resulting proton defects from $p\text{H}_2\text{O}$. In the case of doubly ionized oxygen vacancies $\text{V}_\text{o}^{\bullet\bullet}$, when the process of interaction with water is reduced to a quasi-chemical equation (1), the concentration of proton defects in the structure of the oxide increases with increasing water vapor activity under the law $[\text{OH}_\text{o}^\bullet] \propto p\text{H}_2\text{O}^{1/2}$. For phases with neutral defects, the concentration of protons is proportional to $p\text{H}_2\text{O}^{1/3}$.

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